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Blend

A Fluoropolymer Composite with High Ionic Conductivity

1. Field of the Invention:

The object of the invention is to provide a fluoropolymer ^{blend} composite with high ionic conductivity, more particularly, which is applicable to an electroactive polymer composite (EAPC) membrane ^{having} ~~and the membrane has~~ the merits of excellent thermal resistance, acid-alkali resistance, mechanical strength, curvature, and flexibility ~~etc.~~

2. Background of the Invention:

Following the high-level progress of requirement, the common 3C video photoelectric products (computer, communication, and ^{consumer electronics} ~~consuming electron~~) are expected to continue to become the star industry for Taiwan after she entering the 21st century. The market requirement shows that the product specifications for monitor^s, laptop computer^s, desktop computer^s, cellular phone^s, and other data storage device^s have already developed gradually toward the trends of lightness, thinness, shortness, smallness, and multifunction^{capabilities}. These trends are expected to be widened to all the 3C video products. For the ^{thin} plastic pieces of ~~thin shape~~, especially for the outer shell, the requirement for the characteristics of resistance to sound, vibration, heat, and electromagnetic waves has become a necessity ~~and urgency~~. Nowadays, because of the limitation of materials, the actuator^s of optical, thermal, and electric mechanisms can not fulfill the requirement of ^{the} next generation for extra-lightness, -thinness, -shortness, -smallness, and low energy consumption. The revolutionary EAPC of intelligent composite has the merits of lightness, elasticity, low power consumption, long life cycle, and quick reaction, ~~etc.~~ and is the optimal choice for a brand new actuator. The actuators, manufactured by this material ^{including} ~~such as~~: micro pump^s, optical switch^s, gripper^s, fan^s, optical-valve^s, lens controller^s, focus lens^s, micro-mirror^s, and active noise controller^s, ~~etc.~~ ^{and} may be applied in the products of machine^s, micro device^s, 3C component assembly^s, photoelectric device^s and other artificial muscle for medical treatment ~~and people livelihood~~. In tradition, the most typical ionic polymer for EAPC intelligent composite is Nafion. A membrane made by this material has the cluster of hydrophile property, and this cluster is connected by narrow ionic passage^s, ~~and~~ by which water or

ion is transferred quickly. However, the passage ^{is} easily destroyed to interrupt the transfer due to the dehydration of the material, ^{Also} besides the price of the material is extremely ^{high} expensive, its coming source is not easy to handle, and the manufacture of this material is further very complicated.

5 In order to further apply this kind of material in increasingly precise and miniature electronic products, the research of this field ~~made by more and more people~~ has shown that there are still many shortcomings ~~existed~~.

The US Patent No. 4308359 ^{discloses a limited} has disclosed an application of PVDF-g-SPS, ^(styrene-grafted and sulfonated PVDF) but its property does not fulfill the requirement, so its
10 application is limited.

In a compound method of PVDF-g-SPS mentioned in the literature of Electrochem Acta, 43, NoS, 12-13, p1881~p1890, a PDVF membrane is irradiated under 175KV, 100kGy, then immersed in styrene solution ^{to form a grafted product which is sulfonated} after
to form PVDF-g-SPS. ^{This} circulation, and sulphonated. Its product may be applied in a conduction
15 membrane of hydrogen ion or fuel cell, but it is still necessary to enhance its effect.

In the literature of Materials Research Society Symposium Proceeding Vol. 600, P267, 2000, Materials Research Society, a test piece made by polyvinyl acetate applies Au as an electrode, but it still has the shortcoming
20 of easy ^{breakage} break during swinging.

In the literature of Materials Research Society Symposium Proceeding Vol. 600, P229, 2000, Materials Research Society, a macromolecule electrolyte membrane of Nafion or Flemion with ^{a perfluorinated structure} full fluorine applies Au as an electrode. The membrane may be deflected under the driving of low
25 voltage, but its application field is ^{very} still too narrow, and it is ^{not easy to} uneasy for
change properties changing property and mass production. Besides, the price is expensive and the limitation of its coming source is further a serious problem that
harasses the relative business.

In the US Patent No. 5403675, a macromolecular with the rigid-rod of polyphenyl is sulphonated to make PEM to replace Nafion for reducing the
30 price and ^{maintaining} still keep excellent conductivity. But, the shortcomings of such kind of molecule are: its solubility to water is too large during high ionization; the conductivity is worsened during low ionization; and the

stability is poor.

In ~~the~~ US Patent No. 5,795,496, a sulphonated PEEK replaced^S the Nafion and is made as dense surface membrane for reducing the penetration rate of methanol, and is applied in ~~the~~^a fuel cell. Its shortcomings are that the solubility to water is great for the S-PEEK and the conductivity of the membrane is lowered when the ionization of the dense surface membrane is reduced.

From above description, ^{there is a need} ~~the relative business still has~~ to develop a conductive membrane that has excellent characteristics and competition to drive macromolecular composite electrically for reaching the requirements of high mechanical strength, high conductivity and high stability.

Summary of the Invention

The object of the invention is to provide a fluoropolymer^{blend} composite with high ionic conductivity that may be applied in an electroactive polymer composite (EAPC). The membrane has the characteristics of excellent thermal-resistance, acid-alkali resistance, mechanical strength, curvature, and flexibility, etc., and also has the tensile strength over 250kg/cm².

Another object of the invention is to provide a fluoropolymer^{blend} composite with high ionic conductivity that may be applied in an electroactive polymer composite (EAPC) membrane. The membrane has excellent mechanical performance and may also be cross-linked under the alkaline circumstance of diamine or peroxide for further enhancing its mechanical performance. (polyurethane^{fluoride})

Further object of the invention is to provide a fluoropolymer^{blend} composite with high ionic conductivity that is comprised of PVDF-g-SPS^(styrene-grafted and sulfonated PVDF), PVDF^{blend}, and fluoro- or hydrocarbon-elastomer. The compound membrane may ~~get~~ obtain appropriate mechanical performance and flexibility by proportional adjustment of above components.

In order to achieve above objects, the invention particularly provides a fluoropolymer^{blend} composite with high ionic conductivity that may be applied in an electroactive polymer composite (EAPC) and ~~mainly~~ includes the following components: PVDF-g-SPS, PVDF, and hydrocarbon- or

fluoro-elastomer. The invention is a ^{blend} composite assembled by these three components, that is, PVDF-g-SPS, hydrocarbon- or fluoro-elastomer, and PVDF. After mixing the PVDF-g-PS, hydrocarbon- or fluoro-elastomer, and PVDF with specific proportion and dissolving them in an oily or non-oily solvent of non-proton or proton of high boiling point, the solution is coated on a substrate and is heated to get rid of the solvent afterwards to get a compound membrane. Then, a compound membrane of PVDF-g-SPS may be obtained by sulphonating the aforementioned compound membrane. The obtained compound membrane has excellent properties, such as thermal stability, acid-alkali resistance, good mechanical performance, excellent flexibility, and capability for processing appropriate cross-link for further enhancing the mechanical performance of this membrane.

In addition, there is another characteristic for the compound membrane of PVDF-g-SPS according to the invention. That is, the ^{degree of} grafting rate of the PVDF-g-PS in the process may be adjusted at random, and after it being ^{sulphonated} ~~sulphonated~~, different ^{ionic group content} ~~ionization rates~~ of PVDF-g-SPS may be obtained. The properties of chemical resistance and mechanical performance of the PVDF-g-SPS of high ionization rate can also be enhanced because of adding the hydrocarbon- or fluoro-elastomer, while the increase of adding proportion of hydrocarbon- or fluoro-elastomer may also raise the flexibility of the compound membrane appropriately. Therefore, the compound membrane of PVDF-g-SPS according to the invention may fulfill the functions that can not be obtained by prior arts, that is, its mechanical strength or flexibility can be raised according to the necessity, or both can be fulfilled as requirement at the same time.

Detailed Description of the Preferred Embodiment

The process of the compound membrane ^{blend} composite of fluoropolymer with high ionic conductivity is to contain the ^{sulfonic acid group} ~~proton~~ as the main component for the PVDF-g-SPS. First, the process flow path of the PVDF is to graft the styrene monomer onto the PVDF to become the PVDF-g-PS by the applications of x-ray, electron beam, γ -ray or plasma method. However, appropriate ^{degree of} grafting ~~rate~~ may make the resin keep ^{retain} its original mechanical performance and keep appropriate solubility in solution to facilitate

(defined as: d.o.g. = $\frac{m_1 - m_0}{m_0} \times 100\%$, where m_0 is the mass of PVDF, and m_1 is the mass of grafted PVDF)

following reaction or working procedures. In order to reach the appropriate ^{degree of} grafting ~~rate~~, we may control the amount of monomer usage, kind of irradiator, and time of irradiation to change ^{the degree of} its grafting ~~rate~~ as ^{required} requirement. Then, the PVDF-g-SPS can be obtained by sulphonating the
5 PVDF-g-PS with sulphonating reagents, such as strong sulfuric acid, chlorosulfonic acid or ~~flaming~~ ^{burning} sulfuric acid, etc.

As a general rule, several factors may influence the properties of the resin:

(a) During low ^{degree of} grafting ~~rate~~, although the mechanical property of the ^{ratio (defined as $[m_s - m_d / m_d] \times 100\%$, where m_s is the mass of swelling membrane, and m_d is the mass of dry membrane)} membrane is better, ~~but~~ the containment of ^{sulfonic acid} sulfonate group is low and water uptake ~~rate~~ is also low, so its ionic conductivity is worse.

(b) When the ^{degree of} molar grafting ~~rate~~ of the styrene is higher than 45%, the containment of ^{sulfonic acid} sulfonate group is increased to make better ionic conductivity.
15 But, the membrane formation is ~~become~~ worse, neither is the mechanical property to cause the thin membrane easy to break, so its application is limited greatly.

(c) The membrane made by the PVDF-g-SPS only is difficult ^{to apply} ~~for~~ applying in an electroactive polymer (EAP) material. Although its ionic
20 conductivity and mechanical strength may reach the requirement, ~~but~~ its hardness is too great to get a good flexibility, so even swollen by water, the membrane still can not be driven by external electric voltage due to too great rigidity.

^{The above -} Above-mentioned shortcomings can all be improved by the technique
25 disclosed by the ^{present} invention, which is a ^{blend} composite assembled by three components, that is, PVDF-g-PS, hydrocarbon- or fluoro-elastomer, and PVDF. After mixing the PVDF-g-SPS, hydrocarbon- or fluoro-elastomer, and PVDF with specific proportion and dissolving them in an oily non-proton solvent with high boiling point, the obtained solution is then
30 coated on a substrate and is heated to get rid of the solvent to get a compound membrane. A desired compound membrane of PVDF-g-SPS can be obtained by ^{sulphonating} sulphonating the compound membrane by
aforementioned ^{sulphonating} sulphonating method. The obtained compound membrane of PVDF-g-SPS has following ~~excellent~~ properties:

irradiation of γ -ray, electron beam, x-ray or plasma method. Its ^{degree of} molar grafting ~~rate~~ is preferably between 10% to 100%, but ^{preferably} ~~the best one~~ is between 30% and 65%. The control of this ^{degree of} grafting ~~rate~~ may be determined by the

5 monomer. The appropriate graft following the procedure of ionization may introduce the desired ^{sulfonic acid} sulfon~~yl~~ group that is served as the main source of water absorption for the membrane, also is provided as the main passage of transfer inside the membrane for the ions and water. The resin powder may be ionized directly after being grafted, or ionized after the formation of a

10 membrane by the solvent method. In general ionization method, it applies strong sulfuric acid, ~~flaming~~ ^{burning} sulfuric acid, or chlorosulfonic acid, while the reaction time is determined by the particle diameter, membrane thickness, acid reagent concentration, reaction temperature, and sulphonation rate, etc.

As a general rule, the reaction can be completed within three hours ^{at room temperature}. The

15 ^{degree of sulphonation} ~~rate of sulphonation~~ may be determined by analyzing its containment of $-\text{SO}_3\text{H}$ group by the acid-alkali titration method, ^{the degree of sulphonation being the} ~~percentage of sulfonated phenyl groups (ratio of sulfonated phenyl groups to total phenyl groups).~~

The hydrocarbon-elastomer described in the invention may be acrylic-elastomer, while the fluoro-elastomer may be Viton ^{to be polymer} the polymers of vinylidene fluoride/hexafluoropropylene/tetrafluoroethylene, or the mixture

20 of above-mentioned hydrocarbon- and fluoro-elastomer or different fluoro-elastomers. Wherein, the acrylic-elastomer may be the poly ethyl acrylate or the derivatives of other alkyl, ^{molar average} and its molecular weight is preferably between 100,000 and 300,000, and the best one is between 150,000 and 250,000. The ^{molar average} molecular weight of the fluoro-elastomer is

25 preferably between 80,000 and 2,800,000, and the best one is between 100,000 and 200,000. The adding amount of above ^{elastomers} elastomers is 10~60% of the weight of the entire ^{blend} composite.

The solvent applied in dissolving above-mentioned PVDF, fluoro- or hydrocarbon-elastomer, and PVDF-g-PS is ^{an aprotic} ~~a non-proton~~ solvent with high

30 boiling point, such as: dimethylformamide, 1-methyl-2-pyrrolidone, dimethyl sulfoxide or the mixture thereof. In addition, small amount of ^{static} ~~proton~~ solvent may be added in these solvents, and the preferable temperature for manufacturing the membrane with these solvents is between 20°C and 200°C, and the best one is between 60°C and 120°C. Besides

35 the solvent method, any ^{other} ~~another~~ well-known method for manufacturing the

(copolymer of vinylidene fluoride/hexafluoropropylene from 3M Co.)

membrane may also be applied, such as: thermal press method, rolling-and-winding film method, or extruding method, etc.

Other interface activators may be added as assembling components for above-mentioned membrane, such as: the fluoro-surfactants of FC-430, FC-431, Fc-135, etc. of the 3M company, or the hydrocarbon surfactants of Allyl alcohol-1, 2-butoxylate-block-ethoxylate, etc. of the Aldrich company. These surfactants may facilitate the sufficient and uniform combination among each polymer component to smoothen the membrane easily and are helpful to promote the properties of the membrane.

The materials of the invention have been developed through the molecular simulation and computational analysis by computer for researching the relationships among ^{ionic group content,} ~~ion ionization~~, hydration, movement, and the molecular chemical structure, etc. These researches are beneficial to the molecular structure design for new fluoro-series ionic polymer or other characteristics. Further computational analyses may evaluate the feasibility and properties of the composition of key monomers and/or ionomer with different chemical structure.

To implement the content of the invention in more practical way, several preferable embodiments are presented as following for describing the content of the invention in more detail.

First Embodiment

First, the process for manufacturing the PVDF-g-SPS membrane: add a styrene monomer weighted 20~40 grams of 99.9% purity into the PVDF resin powder (average particle diameter is 0.25~0.40 μ m and Mn \approx 200,000) weighted 30~70 grams, after being agitated, the mixture is irradiated with the intensity of 10~35kGy for proceeding the graft reaction. After being filtered, ^{the graft copolymer thus obtained is extracted with acetic acid ethyl ester in Soxhlet apparatus for 8 hours.} ~~the coarse product is proceeded the Soxhlet extraction with the ethyl acetate (acetic ester) for removing the non reactive monomer or styrene polymer.~~ The obtained solid product is white particle and weighted 60~100 grams, and its ^{degree of} grafting ~~rate~~ is 30~50% ~~per mole~~. Further, the PVDF-g-PS product has no decomposition phenomenon (TGA, 10°C/min) below 400°C. Furthermore, with the 1-methyl-2-pyrrolidone as

solvent, add dry PVDF-g-PS weighted 2~5 grams, poly ethyl acrylate (Mn value is 190,000) weighted 4~8 grams, interface activator FC-431 weighted 0.1~0.5g, and PVDF (Mn value is 200,000) weighted 5~9 grams into the 1-methyl-2-pyrrolidone solvent of 100~300ml. These mixture is agitated continuously under the temperature of 60~90°C until all the components are dissolved. The solution is coated on a substrate to become a membrane of thickness of 30~50 μ m under the temperature range of 80~100°C. Next, the membrane is ^{sulfonated} ~~proceeded the ionic reaction~~ with the chlorosulfonic acid for one hour at room temperature under the circumstance of Nitrogen gas. After being taken out, the membrane is washed twice with ethyl acetate and then is gotten rid of residue acid by washing three times with deionized water and becomes an ionic membrane. Finally, the ionic membrane is dried for three hours in the temperature of 60~80°C to get a desired PVDF-g-SPS membrane.

Wherein, the thickness of the PVDF-g-SPS membrane is 40~70 μ m, and its outer appearance shows ^{pale} as coffee color, and its properties are as follows. (a) Under the analysis rate of 10°C/min shown in TGA, this membrane has excellent thermal stability at the temperature below 200°C, and is gradually decomposed at the temperature above 250°C, while 50% of entire structure is decomposed at temperature of 345°C. (b) After being boiled in the boiling water for 30 minutes, the membrane is taken out from the water and wiped dry. Its water uptake is 20~30% by comparing the weights. (c) The conductivity of the membrane is 0.01 S/cm by testing with the method of alternating impedance.

(water uptake = $\frac{[m_s - m_d]}{m_d} \times 100\%$, where m_s is the mass of swelling membrane and m_d is the mass of dry membrane).

Next, the ^{metalation} ~~sulphonation~~ is under proceeding: immerse this membrane in water solution of 1N sodium hydroxide for 10~14 hours to transfer its inside ^{sulfonic acid} ~~sulfonyl~~ group into ^{sulfonate} ~~sulfonyl~~ sodium group, then again immerse this membrane into the salt solution containing the Pt or Au cations for 18~26 hours to make the Pt or Au cations permeate into the membrane and proceed interchange reaction with the sodium ions, finally a reducing reaction is proceeded by the reducer of anion to get the desired electrode. Wherein, the described reducer may be sodium borohydride or sodium sulfite.

This membrane may be driven under the electric current of 1~3 Volt and 0.1~1.0 Hz and the vibration amplitude may reach 11.5mm in the electrolyte (electrode width is 3mm and electrode length is 30mm). Further, the

vibration amplitude may reach 10mm and the application time may also reach 1500 hr after being packaged by silicone polymer.

Second Embodiment

5 The manufacturing method for the PVDF-g-SPS according to this embodiment is similar to that of the first embodiment, ~~mostly~~. The difference is that a Diak#1 (Hexamethylene diamine dicarboxylate) weighted 0.1~0.3 grams and a Pb_3O_4 weighted 0.2~0.5 grams are added into the ^{blend} ~~composite~~ of PVDF-g-PS, poly ethyl acrylate, and PVDF resin. The
10 membrane made by this solvent method is placed at temperature of 130°C ~170°C for 1~3 hours to generate several cross-links in portion among the PVDF resin, PVDF-g-PS, and poly ethyl acrylate. The membrane according to this embodiment has following characteristics: thickness is 40~60 μ m, water uptake rate is 15~20%, while tensile strength may further
15 reach the value of 300 kg/cm².

Table 1 is an ^{experimental} ~~experiment~~ result comparison between the embodiments according to the invention with commonly known methods. From Table 1, the membrane made simply by PVDF-g-SPS according to ^{the} ~~the~~ prior art obviously can not be driven with low voltage; also it is too weak, easily
20 broken and unable to swing. Further, the membrane made simply by PVDF-g-SPS/PVDF is also unable to be driven by low voltage and unable to swing, although the mechanical performance of the membrane is enhanced, but its flexibility is poor. Therefore, they all can not be applied in EAPC.

However, the membrane composite made by the embodiment ^(5 to 7) ~~5 to 7~~ according to the invention ^(5 to 7) may be driven by low voltage and its thickness is thick enough to swing easily without breaking and its driving time is longer than that of Nafion.

Table 1

No.	Components (gram)	Hydrogen Containment (gram)	Equivalent Weight (gram)	Membrane Thickness (μ m)	Swing Test (5V, 0.5Hz)	Notation
3	PVDF-g-SPS (2.75)	1.0250×10^{-2}	--	110	Unable to swing	Easily broken, mechanical performance poor
4	PVDF (5.21) PVDF-g-SPS (1.47)	5.4963×10^{-3}	1215	75	Unable to swing	Hardness large, flexibility poor
5	PVDF (5.21) PVDF-g-SPS (1.47) Ethyl Acrylate (5.01)	5.4963×10^{-3}	2127	140	Good	Swinging time is longer than that of Nafion 117
6	PVDF (9.38) PVDF-g-SPS (2.21) Ethyl Acrylate (7.52)	8.2463×10^{-3}	2317	225	Good	Swinging time is longer than that of Nafion 117
7	PVDF (6.25) PVDF-g-SPS (2.75) Ethyl Acrylate (5.86)	1.0250×10^{-2}	1449	220	Swinging amplitude is too large.	--

Note: the test piece is 3 cm long and 0.3 cm wide.

In summary, the fluoropolymer ^{blend} composite with high ionic conductivity provided by the present invention may be applied in the electroactive

polymer composite (EAPC). The invention applies the PVDF-g-SPS as the fluoropolymer with high ionic conductivity, this polymer is produced by grafting the styrene monomer onto the main chain of PVDF resin, then ^{followed by sulfonation,} ~~ionized by the sulfonyl group, the ionomer composite~~ ^{polymer blend} is formed by mixing
5 PVDF-g-SPS with the fluoro- or hydrocarbon-elastomer and PVDF resin has following merits:

(a) Excellent ionic conductivity ($> 0.01\text{S/cm}$) at room temperature.

10 (b) Excellent flexibility and stability; this membrane of compound material can be driven electrically and completely under the condition of 1V voltage and 0.5Hz frequency.

(c) If required by practice, this membrane of compound material may further be cross-linked appropriately with ~~compounds of~~ ^{organic} diamine or ^{organic} peroxide for enhancing its mechanical strength that may reach $50\sim 350\text{kg/cm}^2$, while its water uptake rate may reach 5~50%.

15 (d) Stable thermal stability; this membrane of compound material is extremely stable at the temperature below 200°C , and is started to decompose gradually from the temperature above 250°C , while the decomposing temperature for 50% analyzed by the TGA is 345°C .

20 (e) Stable chemical stability; there is no decomposition phenomenon for storing this membrane of compound material in the solution of the range of pH 1~14 for the long term, while heated at the boiling water also for the long term, its flexibility is still maintained at good condition without destruction.

25 (f) Excellent replacement of salt; when this membrane of compound material is applied in the macromolecular composite driven by electricity or fuel cell and the noble metal is served as electrode material or catalyzer, since the salt replacement is good, so it is very important for manufacturing process.

30 (g) The obtained membrane not only has the merit of thick thickness of membrane and good function of driving performance, but also has characteristics of excellent mechanical performance, compact structure, long swinging time, superior flexibility, and long maintenance of good conductivity, etc.

*the known perfluorinated ionic polymer and it is
known to the public.*

(h) The cost of this product is much cheaper than that of ^{common} ~~market and its coming source can be found easily.~~

5 While novel features of the present invention have been described with reference to one or more particular embodiments herein, those skilled in the art will recognize that many modifications and variations of the present invention are possible. Therefore, the scope of the present invention is to be limited only by the following claims.